SEASONAL VARIATION OF THE SOLUTE CONTENT AND THE Sr^{87}/Sr^{86} RATIO OF THE OLENTANGY AND SCIOTO RIVERS AT COLUMBUS, OHIO[1, 2]

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ABSTRACT

The concentrations of sodium, potassium, calcium, and strontium in water samples collected from the Olentangy and Scioto Rivers at Columbus, Ohio, during 1966, have been determined. The water samples were collected at weekly intervals throughout the year and were combined into four-week composites. The average concentrations, weighted according to discharge, and the ranges of variation for each element in the Olentangy River (in units of $\mu g/ml$) were: Na=22.3 (16.6 to 38.5), K=3.3 (2.2 to 4.9), Ca=72.4 (54.4–101.5), Sr=0.923 (0.604 to 1.73). In the Scioto River the concentrations of these elements were: Na=12.2 (5.8 to 20.3), K=3.6 (2.2 to 5.0), Ca=78.8 (53.2 to 96.2), Sr=1.91 (0.954 to 2.79).

In both rivers the concentrations of sodium and strontium decreased linearly with increasing discharge, whereas the concentrations of potassium and calcium did not. The concentration of potassium increased steadily during the summer and reached a peak in the fall. The Sr^{87}/Sr^{86} ratio of the Olentangy River decreased with increasing discharge from 0.7116 to 0.7088 while that of the Scioto River appeared to be constant at 0.7093 ± 0.0003 within the precision of the measurement.

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INTRODUCTION

The chemical composition of water in a stream, particularly during low flow, is related to the chemical and mineralogic composition of the overburden and bedrock in its drainage basin. In inhabited areas, humans may modify the chemical composition of streams by discharging industrial or municipal wastes and by using chemical fertilizers, weed killers, or pesticides which are washed into streams. Knowledge of the seasonal variation of the solute content of streams may be useful in evaluating the importance of the numerous sources contributing to the discharge of a stream and is necessary in monitoring its pollution.

In this study, the concentrations of sodium, potassium, calcium and strontium, as well as the temperature, pH, and the Sr^{87}/Sr^{86} ratios of water in the Olentangy and Scioto Rivers were measured at Columbus during 1966. Our objectives were to obtain information about the seasonal variation of the solute content in the two rivers at Columbus, and to relate differences in their chemical composition to differences in the chemical and mineral composition of the bedrock and glacial deposits in their respective drainage basins. Preliminary reports of this investigation were made by Eastin (1967a, b) and by Eastin and Faure (1967).

Geology of the Drainage Basins

The drainage basins of both rivers above Columbus are underlain by sedimentary rocks of Paleozoic age covered by deposits of till, glacial outwash, and local alluvium, as shown in Figure 1. The bedrock of the Scioto basin above Columbus

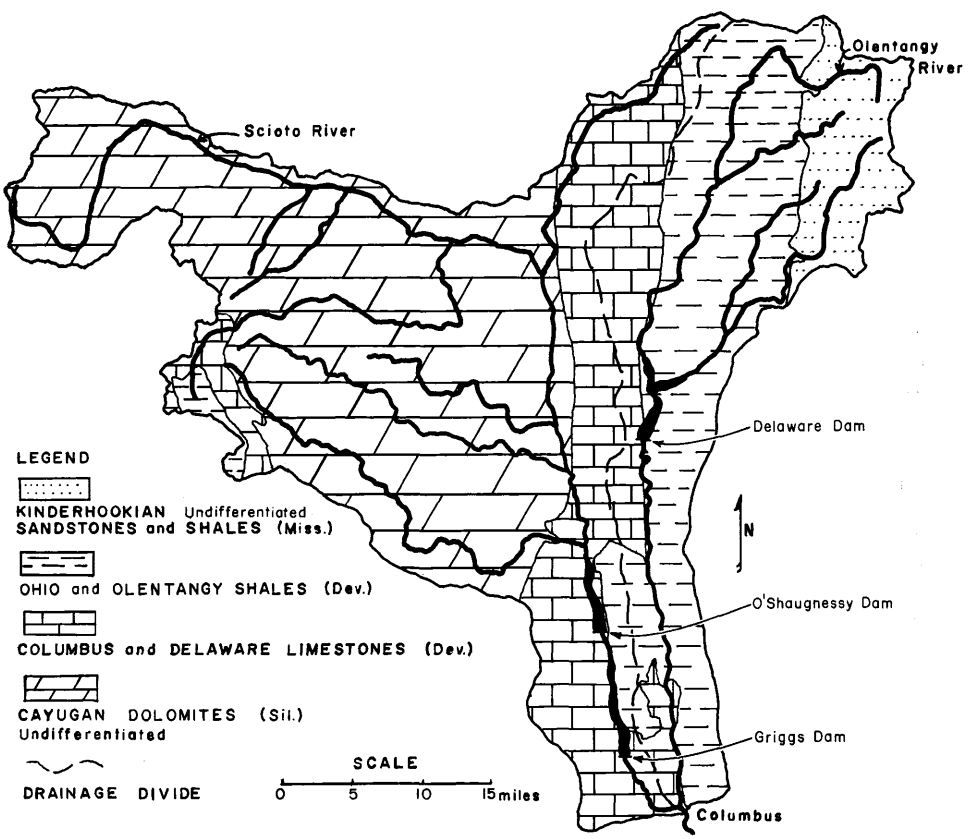

FIGURE 1. Geology of the drainage basins of the Upper Scioto River and the Olentangy River above Columbus, Ohio.

consists primarily of carbonate rocks of Silurian age, but also includes exposures of the Devonian Columbus and Delaware Limestones. The Olentangy River, on the other hand, traverses primarily Mississippian sandstones and shales and the Ohio and Olentangy Shales of Devonian age. The glacial drift, predominantly of Wisconsin age, ranges in thickness from zero to several hundred feet, and averages 50 feet in ground moraine areas. Schmidt (1958, p. 17) showed that more than 80 percent of the pebbles in the till in the vicinity of Columbus are dolomite. The finer fraction of the till generally consists of 15 to 40 percent clay, 20 to 50 percent silt, and 25 to 50 percent sand. The only major difference in the geology of the Olentangy and the Scioto River basins above Columbus is that the bedrock of the Scioto basin is largely carbonate rock of dolomitic composition, while the Olentangy basin is underlain primarily by the Ohio and Olentangy Shales. The composition of the till and gravel deposits appears to be fairly uniform across both drainage basins.

ANALYTICAL PROCEDURES

Samples were collected from the water surface at weekly intervals throughout 1966. The Olentangy River was sampled from a floating boat dock located just west of The Ohio State University's French Field House. Water from the Scioto River was collected in Hoover Park, which is located north of the intersection of Lane Avenue and U. S. Route 33 in Columbus. Approximately 500 ml of water were taken in each sample and were placed in a clean polyethylene bottle. Water temperatures were measured to within 0.1°C at the time of sample collection.

As soon as possible after collection, the pH of the water was determined in the laboratory by means of a Beckman Zeromatic II pH Meter (Model 9604). Buffer solutions of pH = 7.00 and pH = 6.86 were used for calibration of the instrument. A temperature correction was made to allow for the difference in temperature between the water samples and the buffer solutions. The 500-ml water samples were then combined into four-week composites, which were filtered and analyzed for sodium, potassium, calcium, and strontium. The concentration of calcium was measured by titration with EDTA at pH = 12. Sodium and potassium were determined by flame photometry, using a Beckman Model II Spectrophotometer. The concentration of strontium was measured by the technique of isotope dilution, using a spike solution enriched in Sr^{86}. The isotopic composition of the strontium in eight composite water samples was measured with a 60°-sector, 6-inch radius mass spectrometer equipped with a single-filament source (Nuclide Corp, Model 6–60–S). A detailed description of the analytical methods was presented by Eastin (1967a).

DISCUSSION OF RESULTS

The Cation Concentrations

The analytical results are compiled in Table 1 and are plotted in Figure 2. The pH of the water fluctuated between 7.10 and 8.9 in the Olentangy River and between 7.23 and 8.78 in the Scioto River. No correlation between pH and the concentrations of cations was observed. Such a correlation might have occurred had the concentration of cations in the water been at least partially controlled by the absorption of ions by clay minerals. A decrease in pH may cause adsorbed metal ions to be replaced by hydrogen ions, thus increasing the concentrations of these ions in true aqueous solution.

Sodium concentrations in the two rivers at Columbus vary exactly in step (Fig. 2), but the concentration of this element in the Olentangy River (solid line) is consistently higher than that in the Scioto River (dashed line). Two analyses of water from the Olentangy River at Columbus by Hubble and Collier (1960, p. 201) showed sodium concentrations of 10 and 11 ppm for September 1956 and April 1957, respectively. Our analyses of sodium in the Olentangy River in September and April were 31.8 and 29.7 μg/ml, respectively, about a factor of three higher

than for those collected in 1956/57 (μg/ml = ppm x density). This increase may be due in part to the disposal of oil-field brines in Morrow and Delaware Counties. Shaw (1966, p. 15) estimated that, by 1966, approximately 16,000,000 barrels of salt water had been produced as a by-product of petroleum recovery. Much of this brine was disposed of in unlined evaporation pits, from which it infiltrated into the ground and moved in the direction of Whetstone Creek, which is a tributary of the Olentangy River. The consistent difference in the sodium concentrations

TABLE 1

Analytical results for the Olentangy and Scioto Rivers of Columbus, Ohio, in 1966

Composite no. (1)	Na	K	Ca	Sr	(Sr^{87}/Sr^{86}) (3) corr	pH	Discharge (2) $ft^3/sec.$
			μg/ml				
				Olentangy River			
1	30	3.2	81	—	—	—	500
2	39	2.9	92	1.19	0.7116	7.9	205
3	22	2.2	79	0.82	—	8.0	420
4	30	2.6	72	1.21	—	8.4	66
5	19	2.4	72	0.73	0.7086	8.1	601
6	24	3.0	81	0.62	—	8.1	127
7	30	3.3	82	1.54	0.7105	8.2	383
8	17	3.7	54	0.91	—	8.3	1023
9	20	3.7	64	0.98	0.7112	7.7	212
10	32	4.0	74	1.58	—	8.2	21
11	35	4.9	80	1.72	—	8.0	194
12	22	4.1	71	0.84	—	7.8	225
13	17	3.2	69	0.62	—	7.8	1401
14	—	3.1	102	1.41	—	8.0	83
				Scioto River			
1							
2							
3	14	2.5	91	2.12	0.7094	8.02	514
4	16	2.2	96	2.69	—	8.29	201
5	12	2.9	85	2.14	0.7092	8.09	800
6	13	2.7	85	2.11	—	8.33	249
7	16	3.4	74	2.53	0.7088	8.17	407
8	6	3.9	53	0.95	—	8.12	322
9	14	4.2	71	2.27	0.7096	7.95	185
10	18	4.1	68	2.43	—	7.90	47
11	20	4.0	72	2.79	—	8.24	64
12	15	5.0	79	2.11	—	7.87	739
13	9	3.9	74	1.37	—	7.82	1448
14	—	3.1	96	1.97	—	7.84	169

(1) Composite water samples were made by mixing four 500 ml. water samples collected in four consecutive weeks. The time periods represented by each composite are shown in Figure 2.

(2) Average discharge for the days on which water was sampled. Data were taken from "Water Resources Data," Part 1, 1966 of the U. S. Geol. Survey—Water Resources Division. The gaging station for the Olentangy River (#3-2268) is near Worthington. The gaging station for the Scioto River (#3-2210) is near Dublin, below O'Shaughnessy Dam. Discharge data for the period 4 Oct. 1966 to 24 Jan. 1967 were taken from unpublished records of the U. S. Geological Survey, Water Resources Division, Columbus.

(3) Corrected for isotopic fractionation by assuming that $Sr^{86}/Sr^{88} = 0.1194$. The Eimer and Amend isotopic standard was analyzed repeatedly and was found to have $Sr^{87}/Sr^{86} = 0.7083 \pm 0.0002$ (one standard deviation of the mean).

of the two rivers may also be related to differences in the chemical composition of the bedrock. Stout (1941, samples 92, 93, 208, 209, 15 and 224) and Lamborn *et al.* (1938, pp. 20, 34, and 49) reported that the shale in the Olentangy River basin contains considerably more sodium than do the dolomite and limestone in the upper Scioto River basin.

The concentration of potassium in the two rivers behaves quite differently from that of sodium. Figure 2 shows that the potassium concentrations of both rivers increase gradually from low values in March to peak values in October and November. There is no consistent difference in the potassium content of the two rivers, although the Olentangy reaches its peak a month before the Scioto River. If the bedrock controls the potassium content of the river water, the difference in chemical composition of the bedrock should be reflected in a related difference of the potassium content of the two rivers, but this was not observed. Another noteworthy feature is that the potassium concentration appears to be independent of discharge.

Concentrations of calcium fluctuated widely. Except for a brief period from March to May of 1966, the calcium concentration in the two rivers was about the same. Therefore, bedrock cannot be the controlling factor, since the carbonate rocks of the Scioto River basin should have contributed far more calcium to the water than the shale in the Olentangy River basin. The similarity of concentrations suggests instead that the chemical and mineral composition of the till and gravel deposits is far more important than is the bedrock in controlling the release of calcium. The lithology of the till is dominated by carbonate rocks derived from outcrops north and northwest of Columbus. Chemical weathering of these carbonate rock fragments in the till and outwash deposits should contribute calcium equally to the water in the two drainage basins.

The concentration of strontium in the two rivers is unusually high, compared to that of other North American rivers and lakes, as reported by Odum (1957), Skougstad and Horr (1963), and Faure *et al.* (1967). The Scioto River is consistently higher in strontium than is the Olentangy River, as shown in Figure 2. The strontium, like the calcium, is probably derived primarily from weathering of the till and gravel. Feulner and Hubble (1960) concluded that unusually high strontium concentrations in surface water from Champaign County, Ohio, were derived from the Upper Silurian dolomite bedrock and from weathering of celestite ($SrSO_4$) in local till deposits. In the Bass Islands-Sandusky area of Ohio, the Tymochtee, Greenfield, and Lockport Formations of Late Silurian age contain up to 3.5 percent SrO in the form of celestite (Stout, 1941). It is possible that some of this celestite was transported southeastward by the Wisconsin glaciers to the drainage basins of the Scioto and Olentangy Rivers. The more northwesterly Scioto River basin may have received more celestite than did the Olentangy River basin, which would account for the higher strontium concentrations of the Scioto River.

Two similar studies of the relationship of stream chemistry to bedrock geology have been published recently. Angino *et al.* (1969) determined the trace-element content of streams in the lower Kansas River basin, while Müller (1969) reported on the high strontium content of the upper Rhine River and Lake Constance. Anomalous concentrations of strontium relative to calcium in both river systems were attributed in each case to the weathering of celestite. If celestite is also the source of the high strontium content of the Scioto River, a positive correlation with sulfate-ion concentration should be observed, like that demonstrated by Müller for the upper Rhine basin. According to water-quality data published by the Ohio Division of water (1963), surface water in the Scioto River basin above Columbus contains appreciably more sulfate than does water in the Olentangy River basin. The hypothesis that the high strontium content of the two rivers is due to weathering of celestite can be tested in the future.

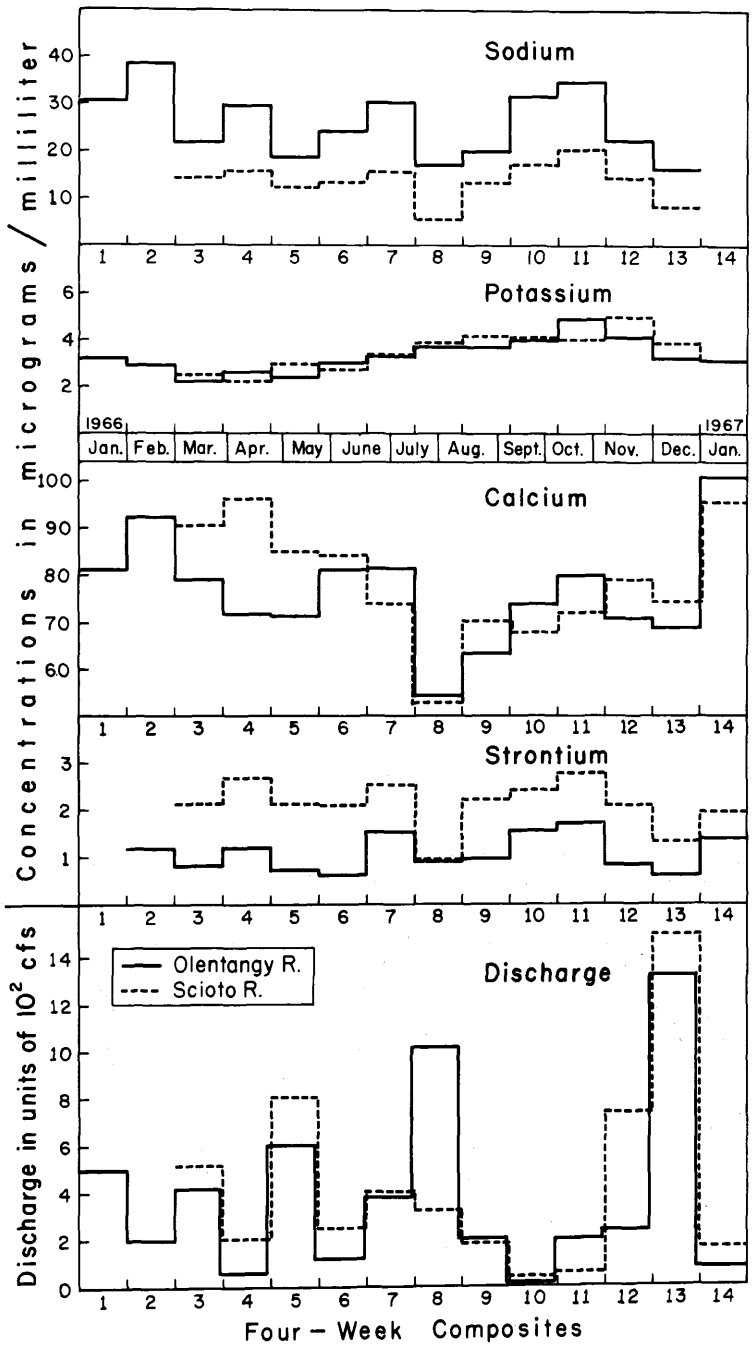

FIGURE 2. Concentrations of Na, K, Ca and Sr in the Scioto and Olentangy Rivers during 1966 at Columbus, Ohio. The concentrations were measured on composite samples which were prepared by mixing water collected at weekly intervals in four-week periods.

In conclusion, the cation concentrations in the Olentangy and Scioto Rivers at Columbus exhibit moderate to large seasonal variations. A single sample is clearly not representative of the water in a river and therefore cannot be used reliably to detect pollution. Table 2 summarizes the range of concentrations and the average concentrations, weighted in accordance with discharge. Sodium, potassium, and strontium vary by factors in excess of two or even three; calcium varies by slightly less than a factor of two. The ratio of concentration of strontium to calcium (Sr x 10^3/Ca) in both rivers has unusually high values. In the Olentangy River the weighted mean value is 12.75 (8.8 to 21.35), whereas in the Scioto River it is 24.22 (17.85 to 38.58). In comparison, the Sr x 10^3/Ca ratio in the oceans is 19.8, but in Lake Superior and in Lake Huron it is only 1.52 and 3.54, respectively (Faure *et al.*, 1967).

TABLE 2

Range of concentrations of Na, Ca, K and Sr in the Olentangy and Scioto Rivers at Columbus, Ohio, during 1966 in units of μg/ml.

Element	Olentangy River			Scioto River		
	Average	Low	High	Average	Low	High
Sodium	22.3	16.6	38.5	12.2	5.8	20.3
Potassium	3.3	2.2	4.9	3.6	2.2	5.0
Calcium	72.4	54.4	101.5	78.8	53.2	96.2
Strontium	0.923	0.604	1.73	1.91	0.954	2.79

The averages were weighted in accordance with discharge for each 4-week composite which are the averages of the discharge values observed on the collecting days. The data for the Olentangy River cover the period Jan. 4, 1966 to Jan. 24, 1967. The data for the Scioto River cover the period Feb. 23, 1966 to Jan. 24, 1967.

Relationship between Discharge and Solute Content

During periods of low flow, highly mineralized groundwater from overburden or bedrock aquifers may be the principal source of water in a stream. During periods of high discharge, on the other hand, the principal source is more dilute surface runoff. Consequently one expects to find an inverse linear relationship between cation concentration and discharge. In this study, the simple mixing model is complicated by the introduction of highly concentrated effluents from sewage-treatment facilities and from industry. If more than two kinds of water are contributing significantly to the total discharge, a plot of cation concentration versus discharge will not form a straight line. Rather, the points will be scattered, and this in itself may be a useful diagnostic indicator of the nature of the supply of a given cation in the stream.

A plot of the concentrations of sodium, potassium, calcium, and strontium versus discharge for the Scioto River is presented in Figure 3. Sodium and strontium form satisfactory straight lines, but potassium and calcium do not. A similar plot made for the Olentangy River leads to the same conclusions, and therefore is not included. For each of the four elements, a linear correlation coefficeint "r" of the best-fit straight line was calculated. The values of r for sodium and for strontium are 0.82 and 0.77, respectively, whereas for potassium and calcium, the values are 0.20 and 0.04. Thus it is clear that no correlation exists between cation concentration and discharge for potassium and calcium. These two elements apparently receive significant contributions from several sources, whereas the sodium and strontium concentrations can be represented more adequately by mixing of only two types of water.

A further complication is the fact that the flow of the Scioto River is regulated by Griggs and O'Shaughnessy Dams (Figure 1). The gaging station whose records were used in this study is located between the two dams. Consequently, when no water was being released by the upper dam, the gaging station recorded an anomalously low discharge. This may have happened during the period covered by composite #8 (July 19–Aug. 2, 1966), for which the concentrations of all cations except potassium were unusually low compared to discharge. The datapoints for composite #8, circled in Figure 3, were omitted from the statistical assessment. The anomalously low discharge recorded for the Scioto River during this period is further illustrated by comparison with the discharge of the Olentangy River in Figure 2. It is the only instance when the discharge of the Scioto River dropped while that of the Olentangy River increased very significantly.

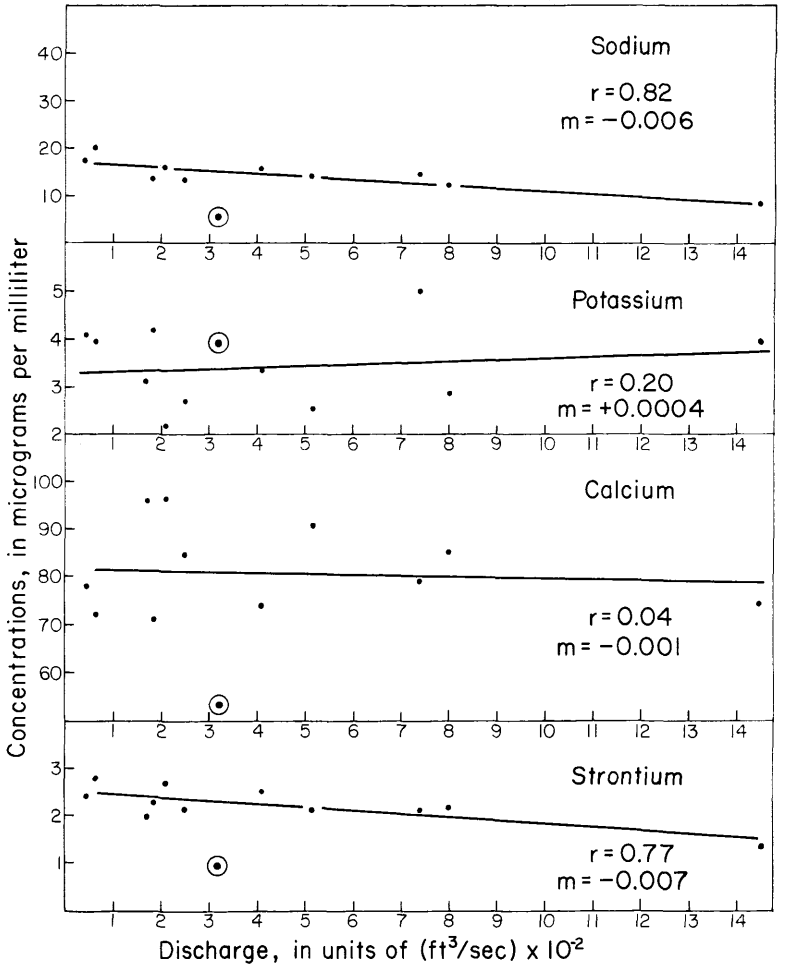

FIGURE 3. Concentration of cations and discharge in the Scioto River at Columbus, Ohio, during 1966. The linear correlation coefficient "r" and the slope "m" of a best-fit straight line have been calculated. The circled points are anomalous because of artificially low discharge.

The Isotopic Composition of Strontium

As a result of the radioactive decay of Rb^{87} to Sr^{87}, the ratio Sr^{87}/Sr^{86} in a rock increases at a rate proportional to its Rb/Sr ratio and the decay constant of Rb^{87}. Chemical weathering of geologically old Rb-bearing rocks releases strontium into solution in the groundwater, whose isotope composition depends on the geologic ages and Rb/Sr ratios of the rocks contributing the strontium. The Sr^{87}/Sr^{86} ratio of surface water is therefore an indirect indicator of the geologic age and chemical composition of the bedrock and overburden in a given drainage basin. For example, Faure *et al.* (1963) found that Sr^{87}/Sr^{86} ratios in surface water and in modern mollusk shells on the Canadian Shield range from 0.712 to 0.726, as compared to 0.709 for sea water. Therefore the strontium in the lakes and rivers of the Canadian Shield is enriched in radiogenic Sr^{87} relative to oceanic strontium.

Measurements of Sr^{87}/Sr^{86} ratios in the Olentangy and Scioto Rivers were made to find out whether differences in the chemical and mineral compositions of the bedrock and overburden in their respective drainage basins were sufficient to produce related differences in the Sr^{87}/Sr^{86} ratio in the water. It was found that,

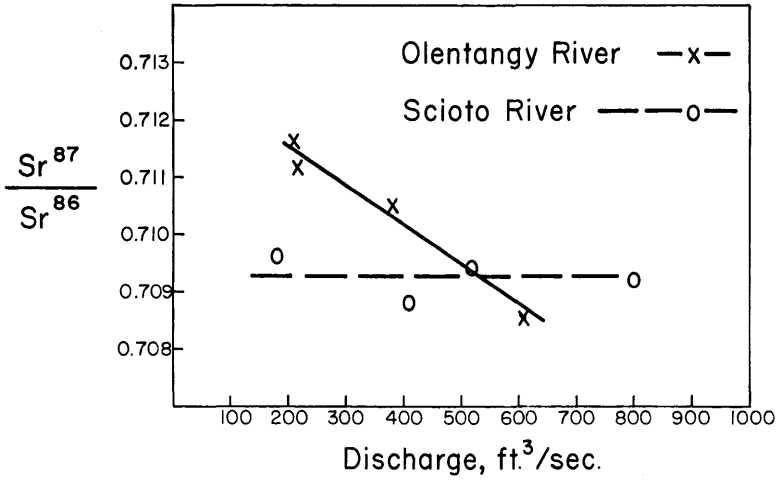

FIGURE 4. Sr^{87}/Sr^{86} ratio and discharge for the Scioto and Olentangy Rivers at Columbus, Ohio during 1966.

in the Scioto River, the Sr^{87}/Sr^{86} ratio varied between 0.7088 and 0.7096 and averaged 0.7093 ± 0.0003 (Table 1). The ratio is constant within the reproducibility of our measurements and is identical to the value reported by Faure *et al.* (1965) for surface water from the North Atlantic Ocean. This suggests that the bulk of the strontium in the Scioto River is contributed by weathering of marine sedimentary rocks. The radiogenic Sr^{87} released by weathering of Precambrian rocks and minerals in the till deposits was not detectable in the water of the Scioto River at Columbus.

In the Olentangy River, Sr^{87}/Sr^{86} ratios ranged from 0.7086 to 0.7116. The variation appears to be real and correlates inversely with discharge, as shown in Figure 4, in agreement with a model in which water is mixed from two different sources which contribute different isotopic varieties of strontium. The excess radiogenic Sr^{87} may originate from the Ohio Shale, which contains detrital rubidium-bearing minerals. This effect is not observed in the Scioto River, where bedrock is predominantly carbonate rock of Silurian and Devonian age.

CONCLUSIONS

Examination of the data in Table 1 clearly shows that the concentrations of some of the major cations in the Olentangy and Scioto Rivers at Columbus fluctuate seasonally by factors of two or three. It is also apparent that the concentrations of cations are not controlled by the chemical composition of the bedrock, but by the weathering of the overburden and by the activities of the human population in the drainage basins. This conclusion is derived primarily from the fact that geochemically similar elements, such as sodium and potassium or calcium and strontium, vary in concentrations more or less independently of each other. Finally there is an interesting inverse correlation between the Sr^{87}/Sr^{86} ratio and the discharge of the Olentangy River.

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